FORMATION OF ADAMANTYLIDENADAMANTANE-1,2-DIOXETANE BY A PHOTOINITIATED ELECTRON TRANSFER REACTION INVOLVING TETRACYANOETHYLENE

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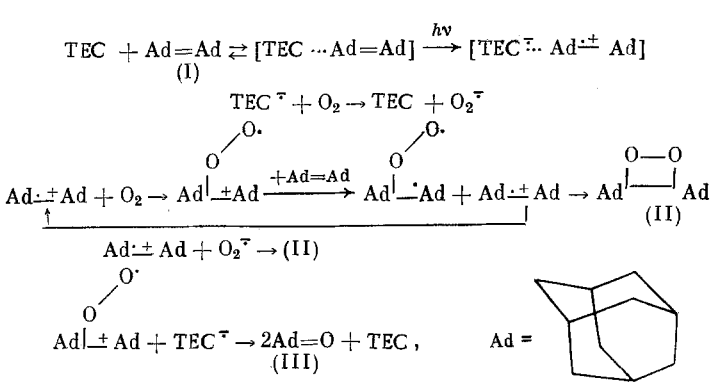
A new oxidative system containing tetracyanoethylene (TCE) and an alkene gives oxetanes. The formation of dioxetane results not from the expected oxidation by singlet oxygen but rather in radical reactions. TCE is a typical electron acceptor and readily forms charge transfer complexes with electron donors [1, 2]. The photoirradiation of such complexes should lead to the generation of the radical-cation of the donor and the TCE radical-anion. Chain reactions of the alkene radical-cations obtained electrochemically in the presence of O_2 may lead to the formation of dioxetanes [3]. Indeed, we have established that the irradiation of solutions of 0.01 mole/liter adamantylidenadamantane (I) and $5\cdot10^{-4}$ TCE in acetonitrile, CH_2Cl_2 and acetone flushed with O_2 at $\lambda > 400$ nm using a DKSSh-1000 lamp leads to the formation of dioxetane (II) and adamantanone (III). After 4.5 h, the conversion of (I) to (II) and (III) was 8% in MeCN, 71% in CH_2Cl_2 and 64% in acetone. The fraction of (II) was 72% in MeCN, 80% in CH_2Cl_2, and 86% in acetone. The synthesis of (II) probably proceeds by a mechanism, in which photoinitiated electron transfer occurs in the first step.



Products in addition to (II) and (III) were not detected. A compound is not formed by the reaction of $(I)^{\cdot+}$ + $TCE^{\cdot-}$, apparently due to the bulky substituents. The alternative mechanism for the formation of (II) involving $^1O_2$ [4] which may be formed upon the quenching of TCE* is unlikely since the conversion of (I) to a 1,2-dioxetane in CH_2Cl_2 and acetone proceeds with identical efficiency although the lifetime of $^1O_2$ differs strongly in these solvents.

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